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Crystalline and amorphous polymeric solid nitrogen

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The structure and thermodynamic functions of solid high-density nonmolecular nitrogen in the crystalline and amorphous phases are studied by a Monte Carlo simulation technique on the basis of the potential model proposed earlier for the cubic gauche polymeric crystal. The solid amorphous state was created by fast melting followed by instant quenching of the crystalline structure. The computed atom-atom distribution functions in such solids are characteristic for amorphous structure. The simulation also reveals the negativity of thermal expansion coefficient of amorphous solid at high density and low temperatures, as was previously found to be the case in the cubic gauche nonmolecular nitrogen crystal. Analysis of the force model shows specific anharmonicity characteristics of the crystalline vibrations responsible for this effect.

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1. Introduction

McMahan and LeSar [1] and Martin and Needs [2] first predicted the existence of a stable polymeric (nonmolecular or atomic) phase of solid nitrogen at zero temperature under pressure. They considered a number of possible threefold-coordinated structures and found the arseniclike $A7$ lattice to be the most stable one at $T = 0$. Later Mailhiot, Yang, and McMahan reported new *ab initio* pseudopotential total-energy calculations [3]. They indicate that a «*cubic gauche*» (cg) distortion of simple cubic atomic structure, in which all nitrogen atoms are threefold coordinated, has an equilibrium total energy lower than that of the arseniclike $A7$ structure mentioned above. According to Ref. 3, the diatomic form of nitrogen should transform into this hypothetical polymeric cg phase at 50±15 GPa and remain the most stable nonmetallic form of nitrogen at higher densities.

This polymeric phase of solid nitrogen, long only discussed by theoreticians [1–3], was recently discovered by experimentalists [4] at ambient temperatures and has also been investigated at elevated temperatures [5]. It was found that this phase very likely has the cg structure and is not crystalline but amorphous.

In our earlier calculations [6–8], we predicted the thermodynamic functions of polymeric nitrogen in the $A7$ arseniclike structure at nonzero temperatures using simple atom-atom potential model. Recently [9] we proposed a new potential model representing the total energy of polymeric nitrogen as a function of both interatomic distances and angles between single chemical bonds attached to each atom. This model was used in prediction of thermodynamic behavior of solid nitrogen in its polymeric cg crystalline phase at high pressures and nonzero temperatures. The calibration of the model was based on the *ab initio* quantum mechanical calculations of Mailhiot, Yang, and McMahan [3] at $T = 0$. We applied this model in Monte Carlo (MC) computer simulations of polymeric solid nitrogen at elevated temperatures.

Our simulations revealed that the polymeric *cubic gauche* crystalline structure of nitrogen would probably exhibit quite unusual high-pressure behavior at elevated temperatures. In particular, *negative* values of the thermal expansion coefficient at high pressures were predicted [9] over a wide range of temperatures. This feature may play an important role in the estimation of the relative stability of different crystalline structures and in the prediction of polymorphous transitions at elevated temperatures. Here we report the extension of the potential model proposed in Ref. 9 to simulation of amorphous polymeric solid nitrogen.

2. Potential model

According to this model [9] the potential energy of N interacting nitrogen atoms consists of two contributions:

$$U_N = \sum_{\text{nonbonded atoms}} \Phi(r_{ij}) + \sum_{\text{bonded atoms}} U(L_{ij}, \theta_i, \theta_j). \quad (1)$$

The first sum in Eq. (1) is taken over all nonbonded atoms, and the second contribution is a partial sum over all nearest chemically bonded atoms, $\Phi(R) = AR^{-13/2}$ is the nonvalence atomic repulsion [4] ($A/k = 3.86\cdot10^5$ K, and k is the Boltzmann's constant). Each atom is involved in three such chemical (valence) interactions. In contrast with our older model [4–6], valence potential U depends here not only from interatomic distances but also from valence angles between chemical bonds, attached to each interacting atom.

Valence interaction of two *single-bonded* atoms U is a function of the chemical bond length L_{ij} as well as the angular variables $\boldsymbol{\theta}_i = \{\theta_i^{(1)},\theta_i^{(2)},\theta_i^{(3)}\}$, and $\boldsymbol{\theta}_j = \{\theta_j^{(1)},\theta_j^{(2)},\theta_j^{(3)}\}$, which represent angles between bonds attached to each atom.

Interatomic valence forces act between pairs of neighboring *single-bonded* atoms only. The corresponding interaction energy $U(L_{ij}, \boldsymbol{\theta}_i, \boldsymbol{\theta}_j)$ was represented by the product of three factors:

$$U(L_{ij},\boldsymbol{\theta}_i,\boldsymbol{\theta}_j) = q(L_{ij},\boldsymbol{\theta}_i)\cdot q(L_{ij},\boldsymbol{\theta}_j)\cdot u_M(L_{ij}), \quad (2)$$

where $u_M(L_{ij})$ is the Morse potential and L_{ij} is the length of a single bond:

$$u_M(L) = D_e[\exp\{-2\beta(L-R_e)\} - 2\exp\{-\beta(L-R_e)\}]. \quad (3)$$

The factors $q(L_{ij},\boldsymbol{\theta}_i)$ in Eq. (2) depend on both the bond lengths and the three plane valence angles $\boldsymbol{\theta} = \{\theta^{(1)},\theta^{(2)},\theta^{(3)}\}$ between three bonds attached to atom (see Fig. 1 in Ref. 9):

$$q(R,\boldsymbol{\theta}) = \frac{2}{1+\exp\{-z(R,\boldsymbol{\theta})\}}\,. \quad (4)$$

Here

$$z(R,\boldsymbol{\theta}_i) = \alpha(R-R_e)^2 + \gamma(c_i-c_e)^2 + \delta(R-R_e)(c_i-c_e) + \varepsilon(1-4c_i)\Delta_i\,, \quad (5)$$

$$c_i = \frac{1}{3}(\cos^2\theta_i^{(1)} + \cos^2\theta_i^{(2)} + \cos^2\theta_i^{(3)}), \quad (6)$$

$$\Delta_i = [\cos^2\theta_i^{(1)} - \cos^2\theta_i^{(2)}]^2 + [\cos^2\theta_i^{(1)} - \cos^2\theta_i^{(3)}]^2 + [\cos^2\theta_i^{(2)} - \cos^2\theta_i^{(3)}]^2. \quad (7)$$

If the atomic configuration is near the equilibrium one, corresponding to minimum energy, all $z(R,\boldsymbol{\theta}_i)$ tend to zero and all $q(L_{ij},\boldsymbol{\theta}_j)$ approach unity. The equilibrium values of the valence angles $(\theta_i^{(j)})_{\text{eq}} = 114^\circ$ in a free cg crystal at zero temperature [3] correspond [9] to $c_e = 0.165$.

The model has seven adjustable parameters: D_e, R_e, α, β,γ,δ, and ε (D_e is the depth of the potential well or equilibrium bonding energy, and R_e is the equilibrium length of a Morse potential for single bond). We used here the same values of parameters: $D_e/k = 35570$ K, $R_e = 1.374$ Å, $\alpha = 12$ Å^{-2}, $\beta = 6.133$, $\gamma = -14.25$, and $\delta = -118$ Å^{-1} as were found in Ref. 9.

This set of parameters reproduces i) the *ab initio* total energy in the *cubic gauche* structure at $T = 0$ as a function of volume, ii) the equilibrium bond angles, and iii) the angular dependence of the total energy within $103^\circ < \theta^{(i)} < 114^\circ$, reported as a result of the sensitivity study by Mailhiot, Yang, and McMahan [3].

3. Monte Carlo simulation of amorphous solid

Computer simulations were carried out using the same computer MC simulation program developed for study of the cg crystal lattice [9] (512 nitrogen atoms and periodic boundary conditions). Initially, all the atoms were arranged within main cell near the sites of a perfect cg lattice (see Ref. 9 for a more detailed description of the cg structure). The MC simulation was initiated with a high initial temperature well above the melting temperature. After some period the initial long-range order disappears and the solid melts. Note that the chemical bonds were fixed during the entirety of the computer experiment and we kept a restriction on allowable distances between bonded atoms (less than 2.5 Å).

Then the system was quenched (the temperature is suddenly reduced to room temperature) and the MC simulation process continues. It was found that after some period of relaxation (after 2000–3000 successful steps per atom) a new quasi-equilibrium state retaining amorphous structure was reached. It keeps the short-range order and threefold valence coordination in first coordination sphere but also has some disorder in bond lengths and directions. This quasi-equilibrium state was studied as a model for the amorphous solid.

During the MC simulation process (namely after each three steps per atom) the values of pressure, internal energy, isothermal compressibility, thermal expansion, and heat capacity were calculated. All of the thermodynamic functions, along with the bond lengths and angles, were averaged over the next 40000 steps per atom to compute the mean values as well as their statistical errors. We also computed the radial atomic distribution functions. Along with the mean values of the angular variables we also monitored the minimal and maximal angles between interatomic bonds.

4. Results and discussion

The atom–atom distribution functions of polymeric crystalline and amorphous nitrogen solid at high density ($V = 6$ cm^3/mol) and two temperatures are compared in Fig. 1. As one can see, the long-range order in the amorphous solid is completely lost, but the short-range first coordination peak formed by chemically bonded atoms is clearly expressed. The second coordination sphere, formed by closest nonbonded atoms, is also present but much less noticeable compared to the crystalline solid. The position of this peak is closely related (see below) to the mean valence angle between single bonds attached to each atom.

In Table we compare calculated values of the thermal expansion α_T and isothermal compressibility β_T coefficients, as well as the isochoric heat capacity C_v, and the mean valence angles $\langle\theta\rangle$ and bond lengths $\langle L\rangle$ of crystalline and amorphous polymeric nitrogen at $T = 300$ and 500 K. As one can see, according to our model, the negativity of thermal expansion should persist in the amorphous state of nonmolecular nitrogen solid at high densities and lower temperatures. It is obviously related to the short-range pyramidal structure formed by neighboring nitrogen atoms. As the mean distance between closest nonbonded atoms increases (see Fig. 1, $T = 500$ K), thermal expansion became less positive.

Table

Some properties of solid nitrogen in the crystalline and the amorphous polymeric phases at $V = 6$ cm^3/mol

Property		300 K	500 K	Δ*
Expansivity α_T, kK^{-1}	Crystalline	−0.018	−0.014	0.002
	Amorphous	−0.011	−0.003	
Compressibility β_T, GPa^{-1}	Crystalline	0.0017	0.0018	0.0001
	Amorphous	0.0015	0.0012	
Heat capacity C_v/R	Crystalline	3.07	3.10	0.003
	Amorphous	3.11	3.08	
Mean valence angle $\langle\theta\rangle$, degrees	Crystalline	106.3	106.2	0.2
	Amorphous	103.6	105.4	
Mean bond length $\langle L\rangle$, Å	Crystalline	1.37	1.38	0.02
	Amorphous	1.52	1.42	

* Estimated statistical error.

It is well known that the anharmonicity of crystalline vibrations is responsible for thermal expansion. The rigorous analysis of all anharmonic contributions to the energy of vibration modes is a complicated task. It requires much effort and is well beyond the scope of this work. However, we have performed an examination of symmetric longitudinal vibrations as the most important kind of crystal vibration in this regard. Our simplified analysis has been performed for the adopted force model within the cg lattice. We took into account that the chemical bonds between atoms are much stiffer than the nonvalence interatomic repulsion. Therefore a symmetric squeezing of the crystal decreases the valence angles between single bonds and correspondingly decreases the distance between nearest nonbonded atoms (see Fig. 1 for the positions of the second peaks near $R = 2.3$ Å).

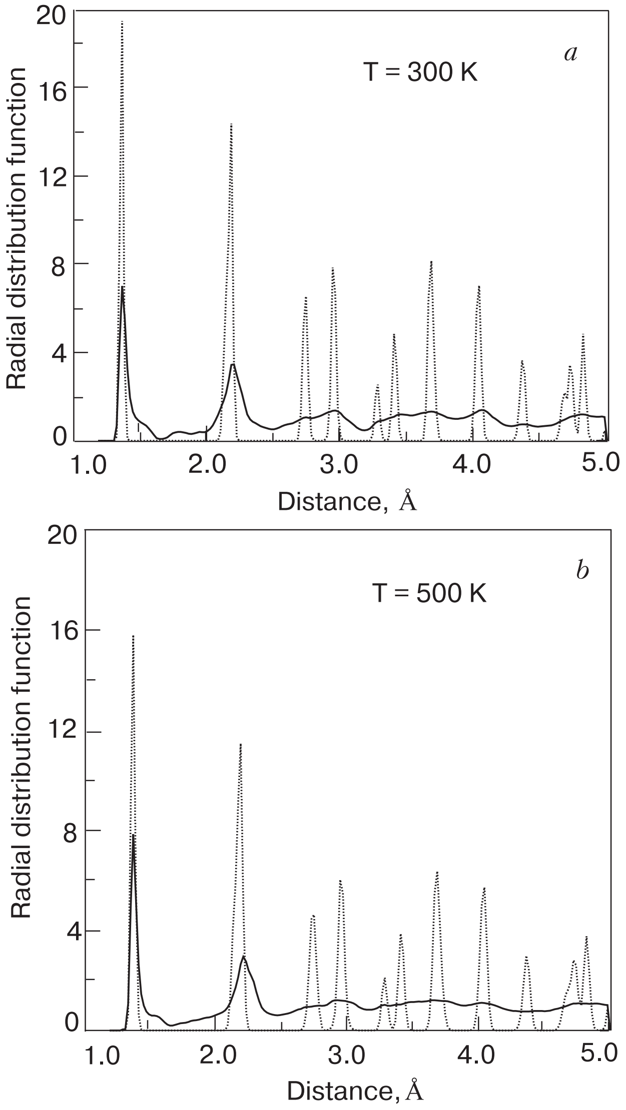

Fig. 1. Radial distribution functions of the amorphous (solid line) and crystalline (dashed line) polymeric nitrogen at 6.0 cm^3/mol and two temperatures 300 and 500 K.

In Fig. 2 we compare the harmonic and anharmonic contributions to the variation of interaction energy with this distance. It is clearly seen that the anharmonic contribution to the interaction energy within our model behaves just opposite to the usual dependence of the potential energy in diatomic molecules, where anharmonicity leads to elongation of the chemical bonds with increase of temperature. In Fig. 2 the interaction energy is more negative at short interatomic distances than its harmonic counterpart. Therefore, as temperature increases, the mean distance be-

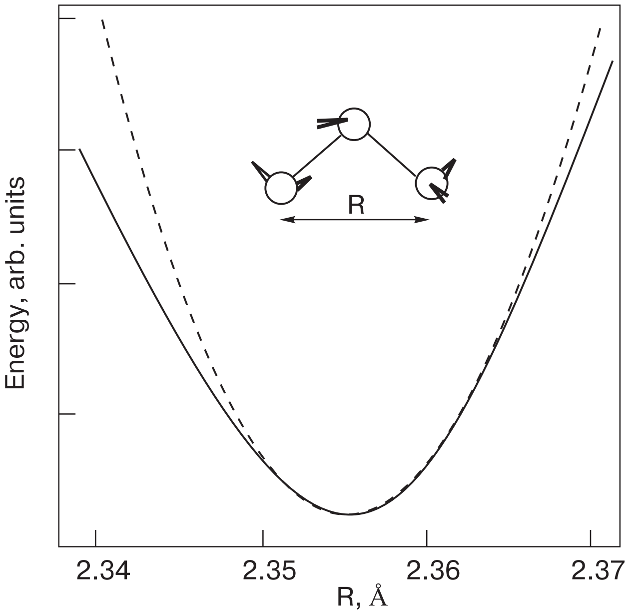

Fig. 2. Potential energy of cg crystalline nitrogen as a function of the interatomic distance between two nonbonded atoms at volume $V = 6.0\ \mathrm{cm}^3/\mathrm{mol}$ (solid line). The harmonic approximation is presented by the dashed line.

tween nonbonded atoms should decrease. We believe that the negative thermal expansion predicted is due to this specific anharmonicity in our potential model.

5. Conclusions

Anomalous structural and thermodynamic behavior of polymeric fourfold-coordinated solids like ice, silicon, carbon etc. has been known for a long time. Negative thermal expansion has also been predicted recently in molecular-dynamic simulations of silicon both in the crystalline and amorphous states [10]. According to our simulation this peculiarity appears in threefold-coordinated structures like polymeric nitrogen only in the helical cg structure and not in the layered $A7$ structure.

The radius of the second coordination sphere in the amorphous cg solid at $T = 300$ K is close to that for the crystalline (see Fig. 1). On the contrary, at $T = 500$ K this radius is markedly shifted to larger distances, which leads to larger mean valence angles and the thermal expansion at 500 K is less negative.

It should be noted that the amorphous state examined in this work as well as the real amorphous nitrogen solid studied experimentally [4,5] is actually not the real thermodynamic equilibrium state. Its properties depend on the frozen structure inherited from the high-temperature melt. Fast quenching of a high-temperature polymeric melt can produce different amorphous states having slightly different properties. We have chosen several samples at $V = 8.04$ and $6\ \mathrm{cm}^3/\mathrm{mol}$ and selected two of them having no broken bonds, i.e. having lengths close to limiting 2.5 Å, see above. We have also continuously monitored the arithmetic mean as well as the maximum and minimum values of the bond lengths and angles between bonds to avoid such bond breaking after quenching. At $T = 300$ K and $V = 6\ \mathrm{cm}^3/\mathrm{mol}$ all the thermodynamic characteristics stabilize quickly and remain constant during the continuance of the computer simulation run. The constancy of the heat capacity computed is another strong piece of evidence of stability of the amorphous state under investigation.

This is not the case at higher temperatures and volumes. We performed several runs at $T = 1000$ K which demonstrate the essential instability of the amorphous solid and gradual recovery of the crystalline structure. Probably much longer MC runs could reach the complete or partial annealing of a stable crystalline structure. But this process is very slow, and such a study is far beyond the limit of our facilities.

1. A.K. McMahan and R. LeSar, *Phys. Rev. Lett.* **54**, 1929 (1985).
2. R.M. Martin and R.J. Needs, *Phys. Rev.* **B34**, 5082 (1986).
3. C. Mailhiot, L.H. Yang, and A.K. McMahan, *Phys. Rev.* **B46**, 14419 (1992).
4. A.F. Goncharov, E. Grigorianz, H.-K. Mao, Z. Liu, and R. Hemley, *Phys. Rev. Lett.* **85**, 1262 (2000).
5. E. Grigorianz, A.F. Goncharov, R. Hemley, and H.-K. Mao, *Phys. Rev.* **B64**, 052103 (2001).
6. L.N. Yakub, *Fiz. Nizk. Temp.* **19**, 531 (1993) [*Low Temp. Phys.* **19**, 377 (1993)].
7. L.N. Yakub, *Fiz. Nizk. Temp.* **21**, 1174 (1995) [*Low Temp. Phys.* **21**, 905 (1995)].
8. L.N. Yakub, *Fiz. Nizk. Temp.* **22**, 222 (1996) [*Low Temp. Phys.* **22**, 174 (1996)].
9. L.N. Yakub, *J. Low Temp. Phys.* **122**, 501 (2001).
10. P. Keblinski, M.Z. Bazant, R.K. Dash, and M.M. Treacy, *Phys. Rev.* **B66**, 064104 (2002).